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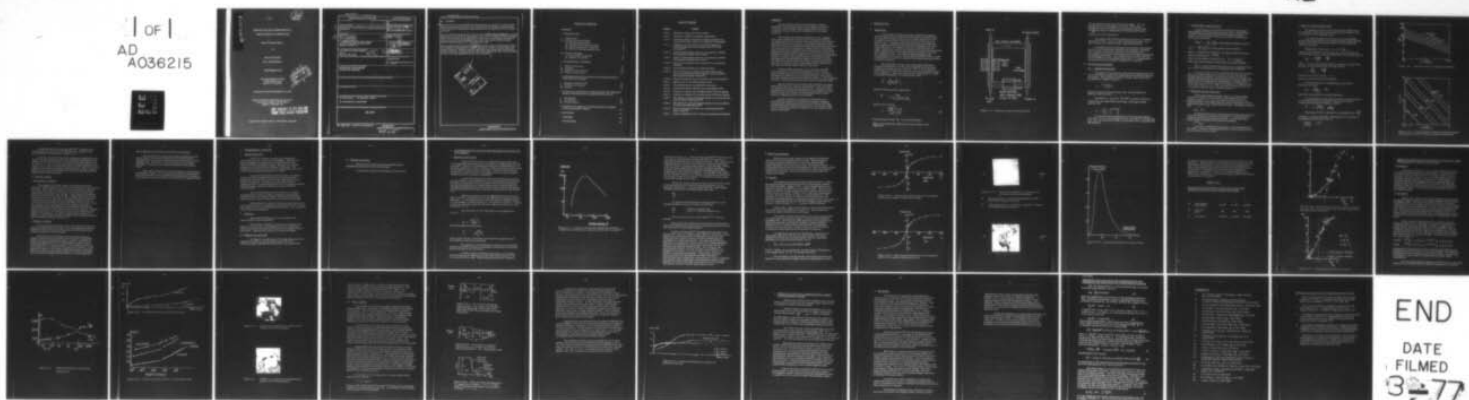
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PREPARATION AND PROPERTIES OF A STABLE METALLIC FERROFLUID.(U)  
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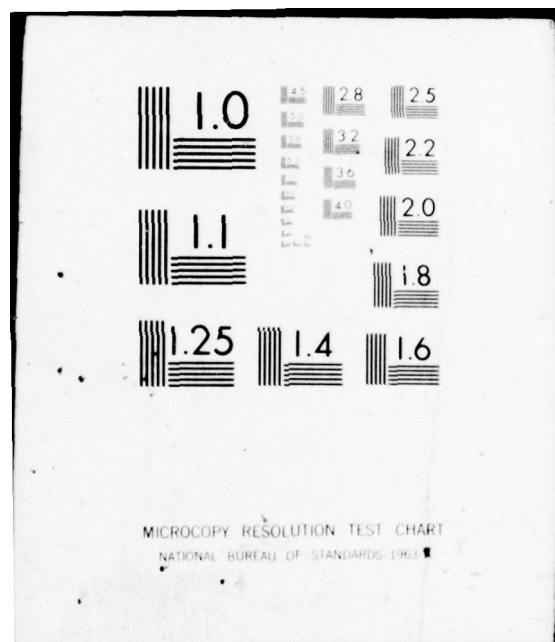
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PREPARATION AND PROPERTIES OF A  
STABLE METALLIC FERROFLUID

Final Technical Report

by

DR S W CHARLES

DR J POPPLEWELL

SEPTEMBER 1976

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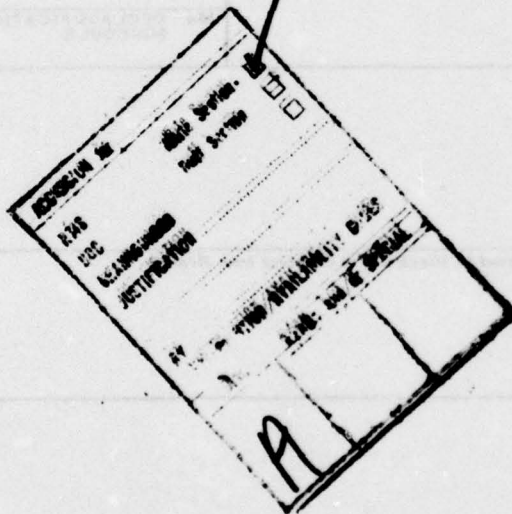
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20. ABSTRACT:

→ The aim of this research work has been to obtain a suspension of small single domain ferromagnetic particles in a metallic carrier stable in high magnetic fields and over a temperature range suitable for its application in an energy convertor.

An ultra stable suspension of iron particles (~~ca 45Å, median diameter~~) in mercury containing 0.7 wt % of tin and approximately 2 wt % of sodium has been produced. This fluid is stable up to 420K and in zero magnetic field over the period of time during which measurements have been made, i.e. approximately one year. To date measurements have not been made above 420K.

Theory predicts that the fluid as described above would be sufficiently stable in a magnetic field gradient of  $10^5$  Oersted/cm to enable it to be used in an energy convertor. However, initial experiments have shown that the effective rate of diffusion of iron particles under the influence of such a field gradient is many orders of magnitude greater than predicted.



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## SUMMARY

The aim of this research work has been to obtain a suspension of small single domain ferromagnetic particles in a metallic carrier stable in high magnetic fields and over a temperature range suitable for its application in an energy convertor.

The mechanisms leading to instability in zero magnetic field, namely diffusional growth of the ferromagnetic particles and agglomeration due to magnetic interactions and van der Waals' type forces have been overcome. The diffusional growth of iron particles in mercury had been effectively eliminated by the presence of tin in the mercury resulting in a coating of the iron particles. Agglomeration due to magnetic interactions has been controlled by ensuring that the magnetic particles are sufficiently small that the Boltzmann energy is great enough to overcome magnetic interactions. Finally, a repulsive interaction between the particles has been introduced into the system by the addition of sodium to mercury. The addition of sodium produces a 'space' charge about the iron particles resulting in a short range repulsive force sufficient to overcome the van der Waals' type forces present.

An ultra stable suspension of iron particles ( $\approx 45\text{\AA}$ , median diameter) in mercury containing 0.7 wt % of tin and approximately 2 wt % of sodium has been produced. This fluid is stable up to 420K and in zero magnetic field over the period of time during which measurements have been made, i.e. approximately one year. To date measurements have not been made above 420K.

Theory predicts that the fluid as described above would be sufficiently stable in a magnetic field gradient of  $10^5$  oersted/cm to enable it to be used in an energy convertor. However, initial experiments have shown that the effective rate of diffusion of iron particles under the influence of such a field gradient is many orders of magnitude greater than predicted.

Further studies are in progress to determine more accurately the properties of metallic ferromagnetic liquids in strong magnetic fields, where the particle content is other than iron and the carrier different from mercury. In this way, those factors required for long term stability in strong magnetic fields may be determined.

# 1 INTRODUCTION

## I. Applications

Ferromagnetic liquids consisting of small ferromagnetic particles dispersed in a metallic carrier fluid have important uses in magnetic low friction seals and in a possible energy convertor. A simple representation of such an energy convertor is given in Figure 1.1.1. A magnetic field acts on a section of the tube and heat is applied in this region to raise the temperature to the Curie temperature of the ferromagnetic particles contained within the liquid. Under these conditions the particles within the fluid experience forces and as they move through the liquid they impart drag to the fluid causing it to flow. If an efficient heat exchanger can be incorporated into the system, then an efficient convertor can be made in which heat energy can be converted to electrical power by means of an M. H. D. Generator.

The usefulness of energy convertors, particularly those designed for portability, say for space applications, is expressed in terms of a weight to power ratio  $w/p$ . The  $w$  in this instance would refer to the weight of fluid and to this must be added the weight of the magnet etc. Hopefully, these factors can be adjusted to make a minimum contribution. It can be shown<sup>1,2</sup> that

$$\frac{w}{p} = \frac{\eta}{\eta_c - \eta} \frac{d_t^2}{H^2} \frac{1}{Z} \quad (1)$$

where the efficiency with regeneration,

$$\eta = \frac{\eta_c}{1 + (2C_o / K \epsilon H T_2) \Delta T_R} \quad (2)$$

and the order of merit,

$$Z = \frac{\left| \frac{dM}{dT} \right|^2 \epsilon^2 K \theta}{16 \pi^2 C_o^2 \rho} \quad (3)$$

$H$  is the magnetic field,  $\eta_c$ , the Carnot efficiency,

$\Delta T_R$  is the temperature difference for heat transfer in the regenerator.

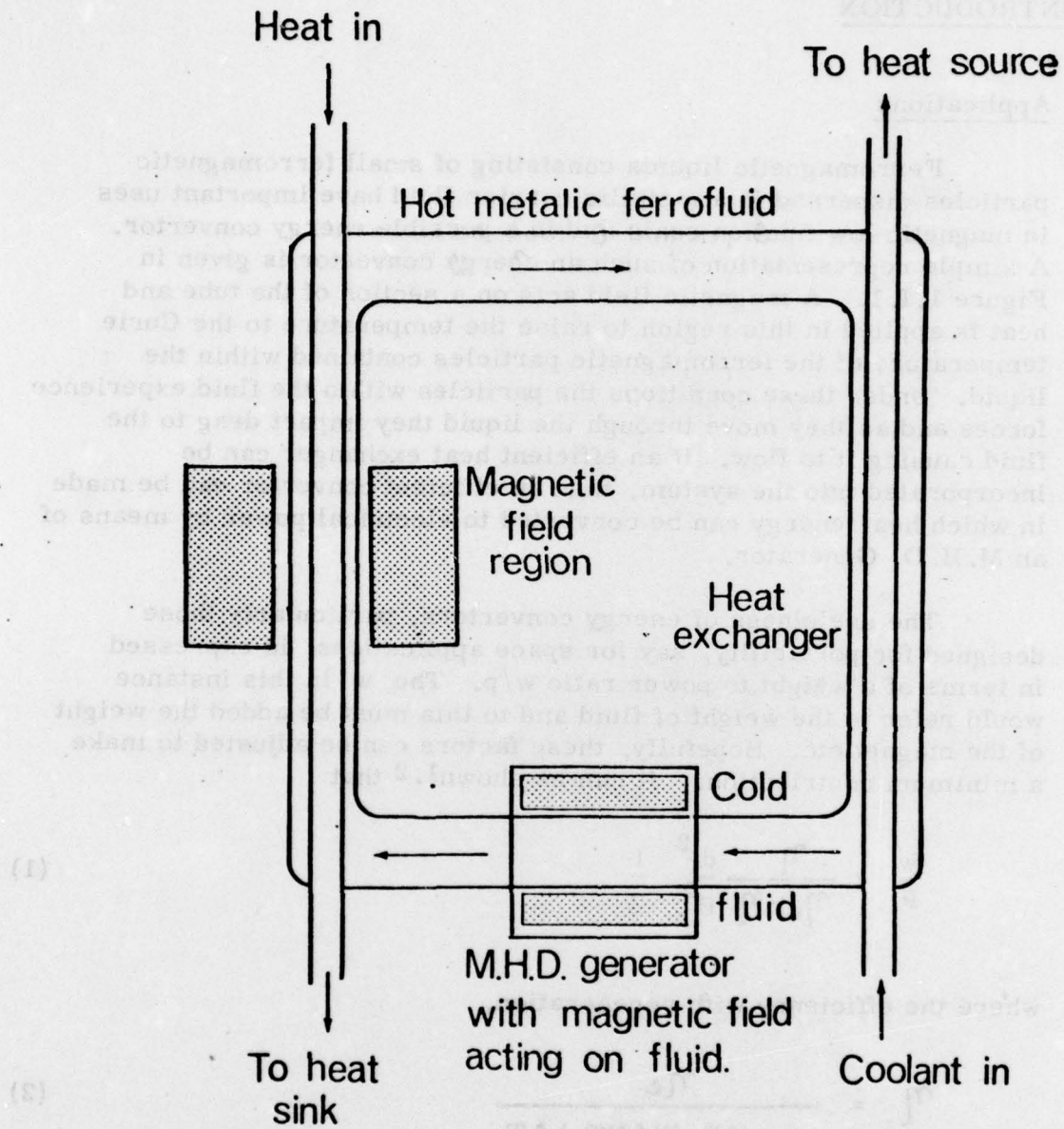


Figure 1.1.1. Schematic energy conversion system

K is the thermal conductivity of the carrier fluid,  $\epsilon$  the packing fraction of the magnetic particles,  $\theta$  the Curie temperature,  $\rho$  the density,  $C_0$  the volumetric specific heat and  $\frac{dM}{dt}$  the change in magnetisation with temperature in the region of the Curie temperature.

It is clear from (1) that for small  $w/p$  a large  $Z$  is needed. Hence from (3)  $\theta$ ,  $K$  and  $\epsilon$  must be large and  $C_0$  small. For high efficiency with regeneration  $\eta$ ,  $\Delta T_R$  must be small.

Although the factors affecting the performance of the energy convertor can be judiciously selected to give optimum conditions, there remains the question of the long term stability of the ferromagnetic liquid under operating conditions of high temperatures and high magnetic fields. The energy conversion system can only be as reliable as the ferromagnetic fluid itself. It is appropriate to introduce the factors leading to instability at this juncture.

## II. Factors affecting stability

### (i) Magnetic Interactions

An estimate of the potential energy of the magnetic interaction can be obtained by treating each single domain ferromagnetic particle as a dipole. The minimum interaction energy, which occurs when the dipoles are aligned is given by

$$U = \frac{-2 m_1 m_2}{r^3}$$

where  $m_1$  and  $m_2$  are the moments, and  $r$  is the interparticle distance; centre to centre.

Assuming  $m_1 = m_2$  and  $m = \frac{4}{3} \pi R^3 I_s$  where  $I_s$  and  $R$  are respectively the magnetisation and radius of the single domain particle, then

$$U = - \left( \frac{2}{r^3} - \frac{4}{3} \pi R^3 I_s^2 \right)$$

In order that thermal agitation may overcome this magnetic attraction, the size of the particles must be such that  $kT$  is comparable to  $U$ . For iron particles at 200°K, the particles must be approximately 30A diameter.

## 2 Van der Waals' type interaction

London-type van der Waals' forces<sup>3</sup> arise from induced dipole-dipole interactions between neutral atoms. De Boer<sup>4</sup> and Hamaker<sup>5</sup> obtained expressions from the potential energy  $U$  between spherical particles based on the London expression for interatomic interaction.

$$\text{Hence } U = \frac{A}{12} \left( \frac{a}{s} \right) \text{ for small distances between spheres}$$

$$\text{and } U = \frac{16A}{9} \left( \frac{a}{s} \right)^6 \text{ for large distance between spheres,}$$

where  $a$  is the particle radius,  $S$ , the shortest distance between sphere surfaces and  $A = \pi^2 n^2 \lambda$

where  $n$  is the number of atoms/cc and  $\lambda = \frac{3}{4} n \nu_0 \alpha^2$   
 where  $\nu_0$  is the ionisation energy and  $\alpha$  is the polarizability.

More recently Lifshitz<sup>6</sup> predicted a longer range dependence on  $S$ , which was subsequently experimentally corroborated<sup>7</sup>.

It must be noted, however, that these theories only consider a dielectric medium between the particles, as in the case for the kerosene based ferrofluids. As the mercury based ferrofluids are metallic then attenuation of the interaction of the van der Waals' type interaction will be expected to be appreciable. Although little is known about van der Waals' forces in ferrofluids, it is apparent that at very short range, i.e.  $\approx 10\text{\AA}$ , the potential energy is large and much greater than that due to magnetic interaction.

## 3 Diffusional Growth of Particles

A theoretical study of particle growth, in a liquid medium has been carried out by Greenwood<sup>8</sup>. Atoms diffuse from the smallest particles, i.e. those with highest surface energy to the larger particles. He predicted that the fastest growing particles are those with a radius  $a_{2m}$ , twice that of the mean. The theory predicted that

$$a_{2m}^3 \propto t.$$

An experimental study of the growth of iron and cobalt particles in mercury has been reported by Luborsky<sup>9,10</sup>. He found that the relationship between the mean particle size  $a$  of the distribution present in the ferrofluid and the time was as follows.

$$a^{4.4} \propto t$$

It should be emphasised that  $a_{2m}$  and  $a$  are not identical but are related. However, bearing this in mind, the two relationships are not inconsistent with each other.

#### 4 Affect of a strong magnetic field

An essential requirement of ferromagnetic liquids is that the suspension of particles remains stable over the period of time it is contained within a magnetic field.

The applied magnetic field exerts a force on the dipolar particles thus inducing them into a steady terminal motion opposed by the frictional force as given by Stoke's Law (assuming near spherical particles).

$$\text{Equating the viscous force } F_s = 3 \pi d \eta_o u$$

where  $d$  is the diameter of the particle,  $\eta_o$  is the viscosity and  $u$  the terminal velocity, with the magnetic force per particle given by

$$F_M = \frac{M \nabla H}{4 \pi} \cdot \frac{\pi d^3}{6}$$

where  $H$  is the field gradient and  $M$  the magnetic moment of the particle, one can determine the terminal velocity

$$u = \frac{d^2}{18 \eta_o} \cdot \frac{M \nabla H}{4 \pi}$$

and hence the particle flux  $N_m = n u$

where  $n$  is the concentration of particles.

The particle flux due to diffusion  $N_D$  is given by the Einstein relationship

$$N_D = \frac{kT}{3 \pi \eta_o d} \cdot \nabla n$$

where  $\nabla n$  is the particle concentration gradient.

By equating the particle fluxes involved in the two processes a relationship between the diameter of the particle and the concentration gradient is obtained as follows

$$d^3 = 24 \left| \frac{\nabla n}{n} \right| \cdot \frac{kT}{M \nabla H}$$

Depending on what is considered an acceptable value of  $\frac{\nabla n}{n}$

a value of  $d$  may be calculated. Rosensweig et al<sup>2</sup> criterion of acceptability was based on a value of

$$\left| \frac{\nabla n}{n} \right| = 1 \text{ cm}^{-1}$$

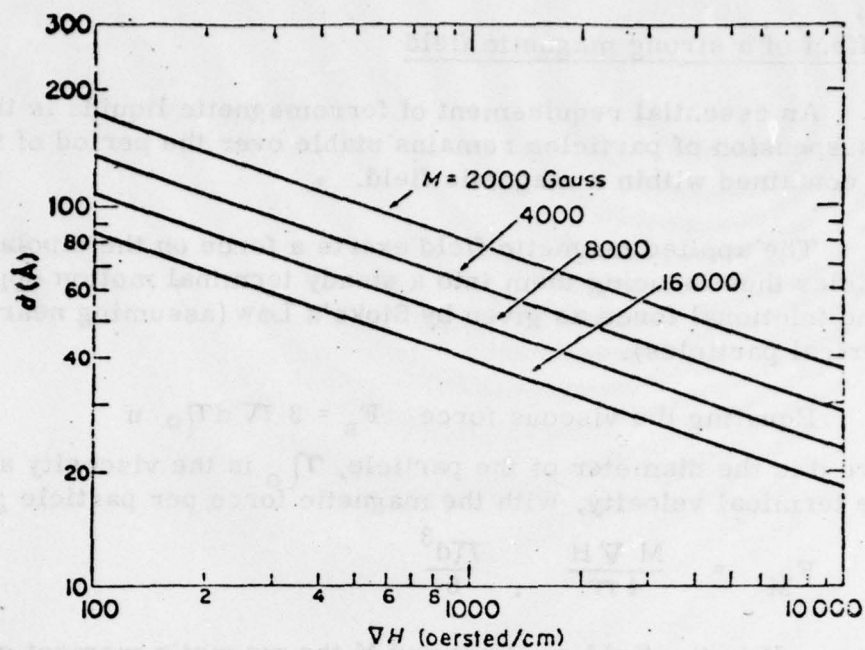


Figure 1.II.1. Separation stability of magnetic suspensions

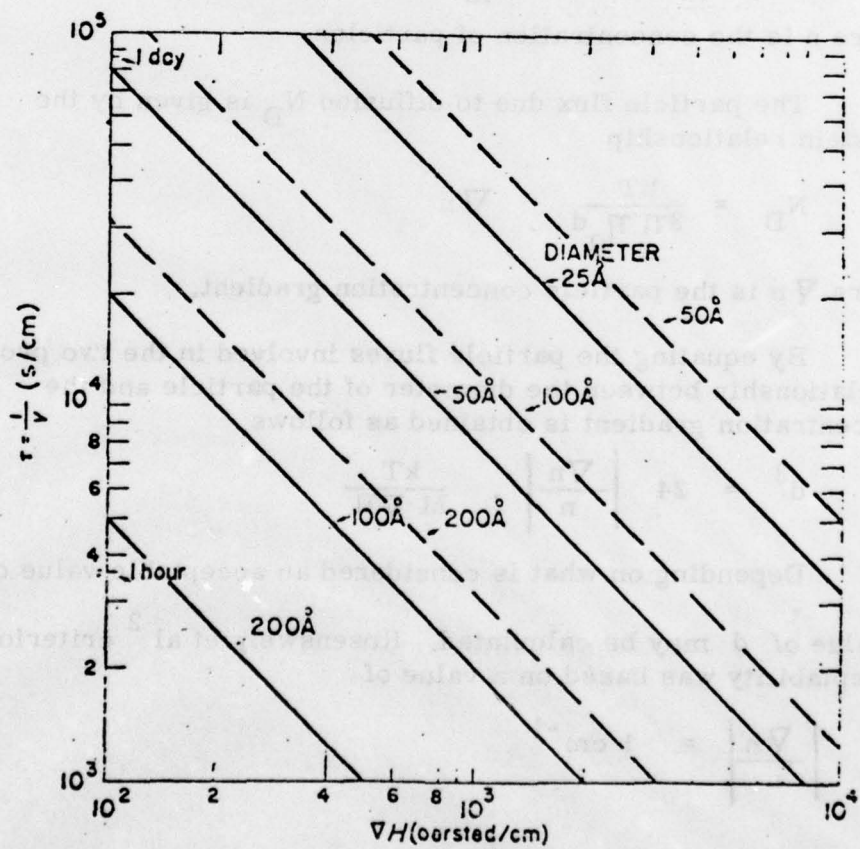


Figure 1.II.2. Terminal motion of spherical magnetic particles in a viscous fluid under influence of magnetic field gradient

Using this value and assuming  $\nabla H \sim 10^4$  oersted/cm then for iron particles (where  $M_s = 21,580$  gauss) the diameter of the particles needs to be about  $15\text{\AA}$ . Figure 1.II.1.

However, the factor which is of even greater importance is the time  $\tau$  for the particles to reach the equilibrium distribution in the presence of  $H \sim 10^4$  oersted/cm. It can be easily shown that the time for this to occur using the above parameters is approximately 1 hour. Figure 1.II.2. This is considerably greater than the time the ferrofluid would be in the field in an energy conversion device. Hence it would appear on theoretical grounds that the presence of high field gradients should not be a serious problem.

### III Particle Coatings:

#### 1 Non metallic ferrofluids

Non metallic ferrofluids consist of suspensions of ferrite particles ( $\sim 100\text{\AA}$  diameter) in carriers such as kerosene, hydrocarbons and water. The problems which give rise to instability, as has just been outlined have been overcome by the introduction of long chain molecules (e.g. oleates) to the carrier. These long chain molecules which are typically of the order of  $10^8$  in length attach themselves to the particle. On close approach of two such particles the long chain molecules push the particle apart, providing an energy barrier of  $\sim 6kT$  to overcome magnetic and van der Waals' forces of attraction. The repulsion is due to the decrease in the number of possible configurations of the adsorbed molecule chains when two particles approach one another. This effect is referred to as 'entropic' repulsion. Diffusional growth of such particles in these carrier fluids does not appear to be significant. The effect of high magnetic fields on the stability of such suspensions does not appear to be inconsistent with the theory outlined previously (Section II4).

#### 2 Metallic ferrofluids

The use of long chain molecules to overcome the mechanisms leading to instability is not possible, since such molecules cannot be dispersed in liquid metallic carriers because of differences in the bonding in polymers and liquid metals.

Clearly there is no problem in overcoming the effects of magnetic attraction of the particles since this can be controlled by keeping the particles sufficiently small. However, the effects of diffusion and aggregation due to van der Waals' forces have to be treated differently. Previous workers<sup>11</sup> have studied the effect of metal additives on the stability of iron particles in mercury. It was found that a metal e.g. tin, which formed intermetallic compounds with the iron and was only slightly soluble in the mercury provided some protection by coating the iron particles. In this way growth

due to diffusion was markedly reduced but not eliminated.

The presence of a coating may modify the magnitude of the van der Waals' force between particles but attraction between particles due to these forces will always be present to some extent, coating or not. Therefore, in order to produce an ultrastable ferrofluid, a means of overcoming this attractive force must be found.

This report presents the results of studies on mercury based ferromagnetic liquids. The results indicate that the van der Waals' forces of attraction can be countered by a repulsive force leading to the preparation of an ultrastable mercury based ferromagnetic liquid.

## 2 EXPERIMENTAL METHODS

### I Sample Preparation

All the ferromagnetic liquids were prepared by electrodeposition into mercury or tin amalgam. The mercury and tin amalgam were supported on a steel cathode for the majority of the ferromagnetic liquids. However, in the latest preparations the steel has been replaced by platinum. The change was made because the steel was causing seeding out of the iron due to its magnetisation by the A.C. field.

A variety of electrolytes have been used. An aqueous solution of ferrous ammonium citrate was used in the initial preparations but this electrolyte has been replaced by Ferrous chloride in methanol. The use of this latter electrolyte in conjunction with a reciprocating surface stirrer overcame problems with polarisation, deposition efficiency and the actual  $\text{Fe}^{2+}$  current density.

The electrodeposition cell was seated on a solenoid, producing an A.C. field, in order to agitate the iron particles as they formed at the cathode surface. This agitation promoted dispersion of the iron particles within the mercury/tin amalgam.

Most studies were made on liquids containing 5% by wt of iron in mercury which corresponds to a magnetisation of  $\sim 5 \text{ emu/g}$ . Above 8% by wt of iron the liquid becomes a slurry.  $\frac{1}{2}$  ml of mercury was used in each preparation.

### II Additives

Approximately 0.7% by wt of tin was added to the mercury prior to electrodeposition.

The addition of sodium to a mercury/tin amalgam was always carried out after electrodeposition of the iron particles. This was necessary because of the reaction of the sodium with the electrolyte. Approximately 2% by wt of sodium was added.

### III Magnetic measurements

All magnetic measurements of the hysteresis loop of the sample were made at room temperature and 77°K with a vibrating sample magnetometer constructed in our laboratories.

## EXPERIMENTAL METHODS

### 1. Sample Preparation

#### IV Electron microscopy

The particle size distribution was studied using an AEI EM6G transmission electron microscope.

A microprobe analysis of the samples was also made.

A variety of electrolytes have been used. An aqueous solution of ferric ammonium citrate was used in the initial preparations but this electrolyte has been replaced by ferric chloride in hexamethylenediamine. The use of this latter electrolyte in conjunction with a reciprocating surface stirrer overcame problems with polarization, deposition efficiency and the actual  $Fe^{2+}$  current density.

The electrodeposition cell was sealed on a vacuum manifold in an A.C. field in order to facilitate the iron particles as they formed at the cathode surface. This reaction promoted dispersion of the iron particles within the mercury in solution. Most studies were made on liquids containing 0.5 wt. of iron in mercury which corresponds to a concentration of  $\sim 2 \times 10^{-4}$  mole/l. Above 2% by wt of iron the liquid becomes a slurry. A dilute mercury was used in each preparation.

### II. Additives

Approximately 0.1% by wt of the was added to the mercury prior to electrodeposition. The addition of sodium to a mercury/iron amalgam was always carried out after electrodeposition of the iron particles. This was necessary because of the reaction of the sodium with the electrolyte. Approximately 2% by wt of sodium was added.

### III. Magnetic Measurements

All magnetic measurements of the hysteresis loop of the sample were made at room temperature and 150K with a vibrating sample magnetometer connected to our laboratories.

### 3 DETERMINATION OF PARTICLE SIZE DISTRIBUTION IN MERCURY AS A CARRIER

#### 1 Magnetic measurements

Previous interpretations of magnetic measurements taken on ferromagnetic suspensions have been based on a single volume particle size theory. However, a knowledge of the particle size distribution is of particular importance in that it enables a realistic evaluation of the results of the magnetic measurements to be made. In addition this knowledge enables one to obtain a better understanding of the processes leading to instability of the ferromagnetic suspension.

A particularly convenient method of determining the particle size distribution in a ferrofluid relies on in situ magnetic measurements. Removal of the particles from the metallic carrier is not only difficult but raises the question as to whether the particles removed reflect the distribution within the carrier and whether in the process of removing the particles the particle distribution is in some way disturbed. (See Section 3.II).

Spherical particles of iron at 293K with diameters less than 60Å, and at 77K, with diameters less than 40Å exhibit superparamagnetic behaviour, i.e. the magnetisation curve will follow the Langevin formula for paramagnetic materials and have no coercivity or remanence. Analysis of such curves is one method by which the range of particle sizes can be determined. (12, 13)

The expression for the initial slope of the magnetisation curve is

$$\frac{I}{H} = \frac{4 \pi I_s^2 r^3}{9kT}$$

and for the approach to saturation

$$\frac{I}{I_s} = 1 - \frac{3kT}{4 \pi I_s r^3 H}$$

where  $I$  and  $I_s$  are the magnetisation and saturation magnetisation of the magnetic constituents respectively.

The approach to saturation gives an estimate of the smaller particle size whilst the initial susceptibility is determined by the larger particles present in the distribution.

A further means of obtaining information concerning the particle sizes may be obtained from coercivity measurements at 77K, i.e. when the fluid is solid. These measurements may be compared

# DETERMINATION OF PARTICLE SIZE DISTRIBUTION IN MERCURY AS A CARRIER

## Magnetic measurements

The above distributions of magnetic moments when the ferromagnetic measurements have been based on a particle size theory, however, a knowledge of the particle size distribution is of particular importance in that it enables a realistic evaluation of the results of the magnetic measurements to be made. In order to achieve this, one must obtain a better understanding of the process of the distribution of the ferromagnetic moments.

A particle's magnetic moment is determined by the particle size distribution in a ferromagnetic material. The particle size distribution is a function of the particle size and the particle size distribution is a function of the particle size. The particle size distribution is a function of the particle size and the particle size distribution is a function of the particle size. The particle size distribution is a function of the particle size and the particle size distribution is a function of the particle size.

The particle size distribution of iron at 293K with diameters less than 1000 Å, and at 77K with diameters less than 100 Å, are shown in Figure 3.1.1. The particle size distribution curves will follow the same general trend, i.e. the particle size distribution curves will follow the same general trend. The particle size distribution curves will follow the same general trend, i.e. the particle size distribution curves will follow the same general trend.

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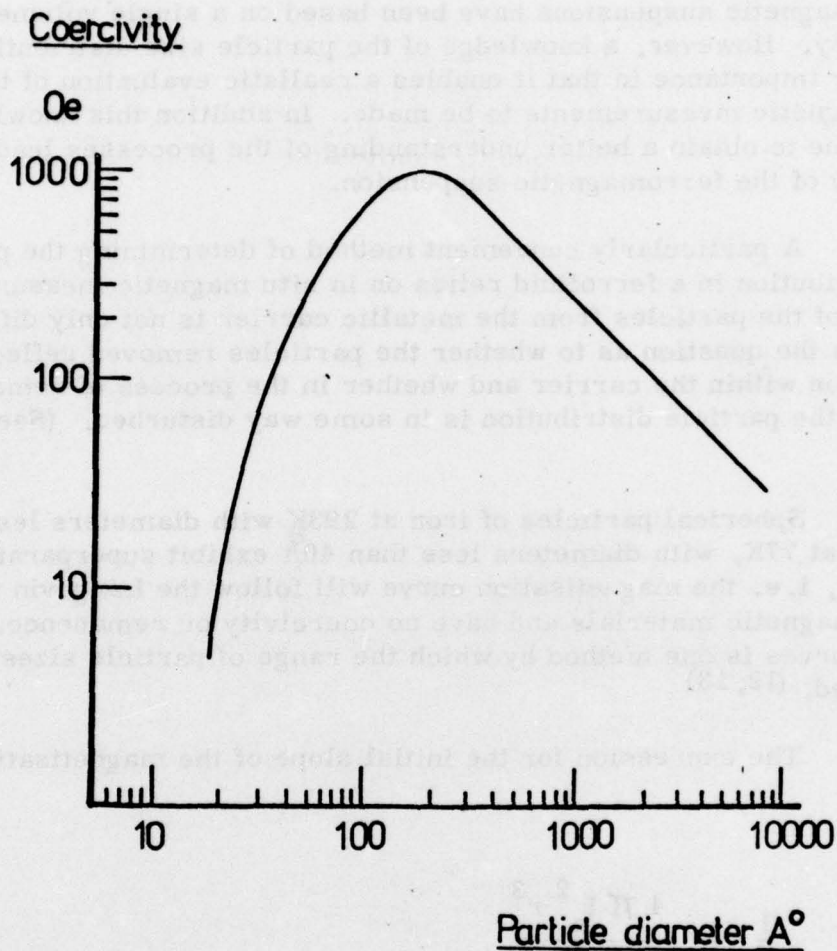


Figure 3.1.1. Change in coercive force with particle diameter of spherical iron particles as measured at 77K, after Luborsky<sup>(14)</sup>

$$\frac{1}{H} = \frac{1}{H_0} + \frac{1}{H_1} + \frac{1}{H_2} + \dots$$

where  $H_0$  and  $H_1$  are the magnetization and saturation magnetization of the magnetic constituents respectively.

The approach to saturation gives an estimate of the number of particles present in the distribution.

A further means of obtaining information concerning the particle size may be obtained from coercivity measurements at 77K, when the liquid is solid. These measurements may be compared

with the curve Fig. 3.I.1. determined by Luborsky<sup>(14)</sup> which shows the coercivity at 77°K against the median diameter of the particle in a particle distribution of iron particles in mercury. For small spherical single domain particles the coercive force increases with particle size and reaches a maximum value of  $2K/I_s$  where  $M_s$  ( $M_s = 4\pi I_s$ ) is the saturation magnetisation and  $K$  the crystalline anisotropy constant. An experimental value greater than that given by  $2K/I_s$  would indicate some particle elongation. A knowledge of the median particle diameter enables one to monitor the particle size distribution for changes through particle growth; an increase in its value could indicate that growth is occurring.

Remanence values may also be used to determine the fraction of the particles which lie above the superparamagnetic size at a particular temperature. It has been shown that, for single domain, randomly oriented non-interacting prolate spheroids

$$\frac{2I_R}{I_s} = 1$$

If a particle size distribution containing both ferro - and superparamagnetic particles is being measured then

$$\frac{2I_R}{I_s} = \text{fraction of particles with radius } > \text{ superparamagnetic size.}$$

This technique has been used by Weil<sup>(15,16)</sup> with some success.

Some idea of the actual form of the particle size distribution may also be obtained from experimental measurement of the coercivity and remanence of a fine particle system.

Kneller and Luborsky<sup>(17)</sup> investigated the behaviour of the coercive force ( $H_c$ ) and remanence ( $M_r$ ) with  $D_v$ , the median particle diameter for a system of small iron particles in mercury, and interpreted their results in terms of a theory derived upon the assumption of a single particle size. The experimental data was obtained by varying  $D_p$  (the critical diameter for superparamagnetic behaviour) by changing the experimental temperature and  $D_v$  by diffusional growth over a period of time. For  $D_v \leq D_p$ , the experimental variation of  $H_c$  with  $D_v$  differs markedly from the prediction of the theory. For the variation of  $M_r$  with  $D_v$ , the deviation is even more pronounced. Computations assuming different particle size distributions have been undertaken. Details of the theory behind these computations are given in Appendix I. The results of these computations are presented in section (3.III) together with values of the upper and lower limits of the particle distribution calculated from the magnetisation curves.

## II Electron microscopy

Electron microscopy enables one to observe the particles removed from a ferromagnetic fluid directly. Unfortunately the processes by which the particles are removed, namely either rapid evaporation of the mercury carrier or direct extraction of the particles from the surface of the liquid, are likely to result in either a disturbance of the particle size distribution or a non representative sample of the particles. Therefore such observations need to be treated with caution.

## III Results

The magnetisation curves shown in Figures 3.III.1., 3.III.2., are typical of the curves obtained for all the 'as prepared' metallic ferromagnetic fluids. Figure 3.III.1. shows a magnetisation curve taken for a sample at 293°K (i.e. as the liquid state). This curve is typical of that of a superparamagnet in that it indicates the absence of remanence and coercivity. Figure 3.III.2. shows the magnetisation curve for the same sample, at 77°K, i.e. in the solid state. The existence of a coercive force of 120 Oe at 77°K indicates that the particles are predominantly non-superparamagnetic at this temperature. In fact, by comparison with the coercive force versus median particle diameter curve in Figure 3.I.1., a radius of 40 Å is obtained.

Table 3.III.1. gives a list of typical particle sizes determined from these curves as explained in section 3.I. Also included are values determined from electron microscopy.

The values obtained from electron microscopy measurements are bigger than those predicted (Figure 3.III.3) from the magnetic measurements. Apart from possible disturbance of the particle size distribution and non representative samples, a further possible explanation for the larger values is the presence of a coating of mercury about the particles. Evidence from microprobe analysis of clusters of particles indicates the presence of mercury.

As regards the particle size distribution, many forms of distribution were tried, but the form which results in the most satisfactory fit with experimental magnetic data is a log normal distribution of volume fraction (Figure 3.III.4).

$$f(x) = \exp \left( -(\ln(x/m))^2 / 2 \sigma^2 \right) / x \sigma \sqrt{2\pi}$$

where  $x = D/D_0$ .  $D_0$  is a parameter characterising the distribution,  $m$  the median value, and  $\sigma$  the standard deviation.

The variations of  $H_C/H_K$  and  $M_r$  with  $D_V/D_P$  computed from equation (1) (see Appendix ) using a log normal distribution of volume

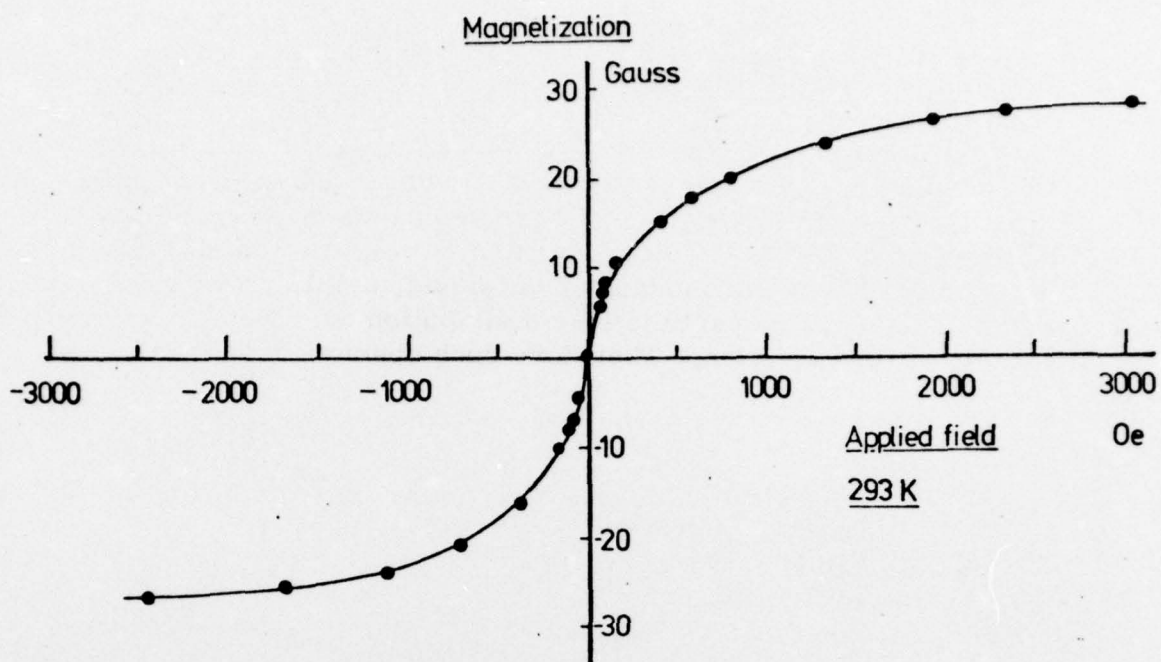


Figure 3.III.1. Typical magnetisation curve for 'as prepared' metallic ferromagnetic liquids taken at 293K

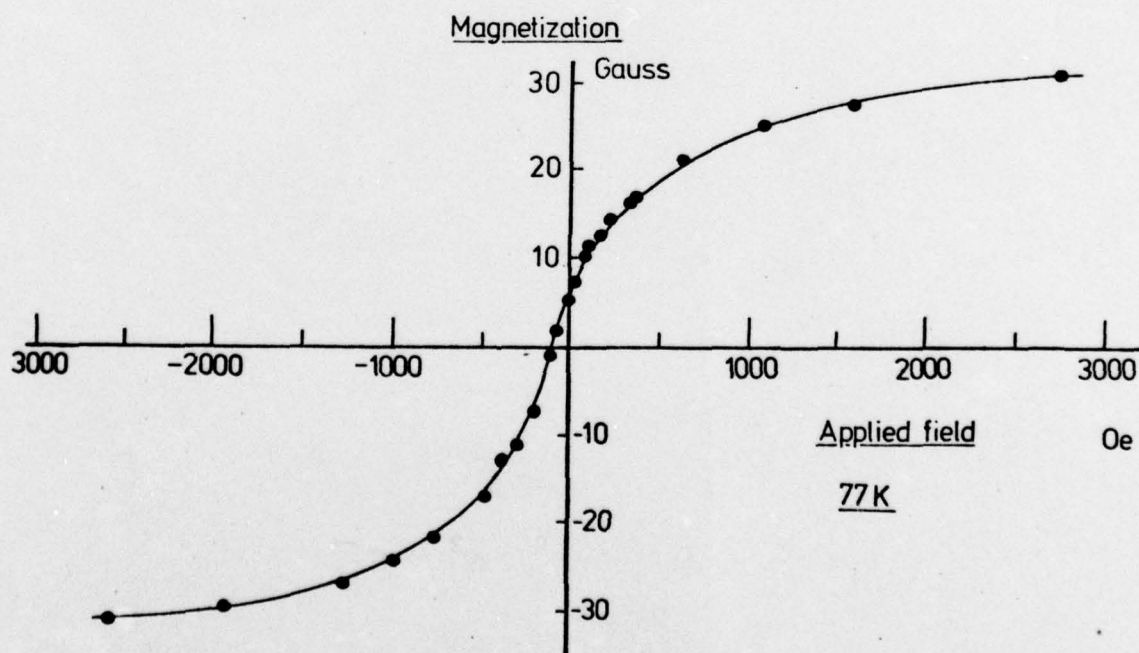


Figure 3.III.2. Typical magnetisation curve for 'as prepared' metallic ferromagnetic liquids taken at 77K

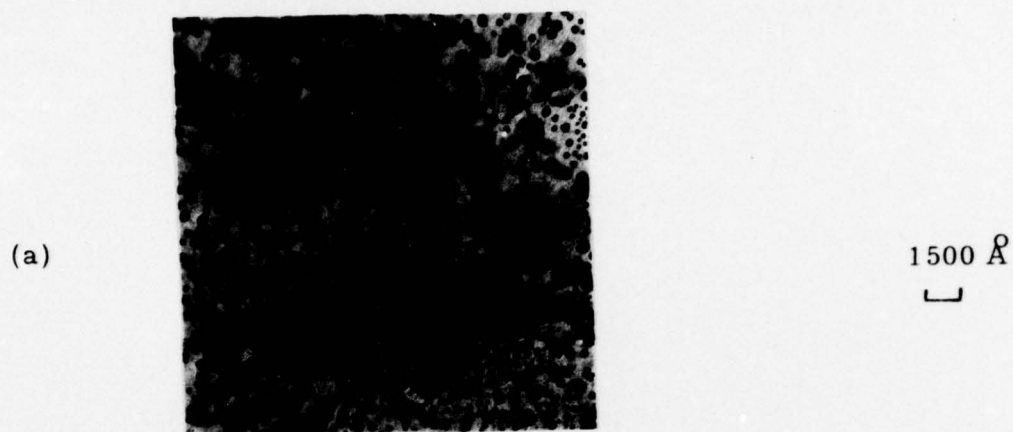


Figure 3.111.3. Electron micrographs of 'as prepared' iron particles in mercury tin/amalgam.

- (a) 25K magnification: mercury encapsulating individual particles and groups of particles
- (b) 100K magnification: most mercury evaporated: presence of individual particles observed.



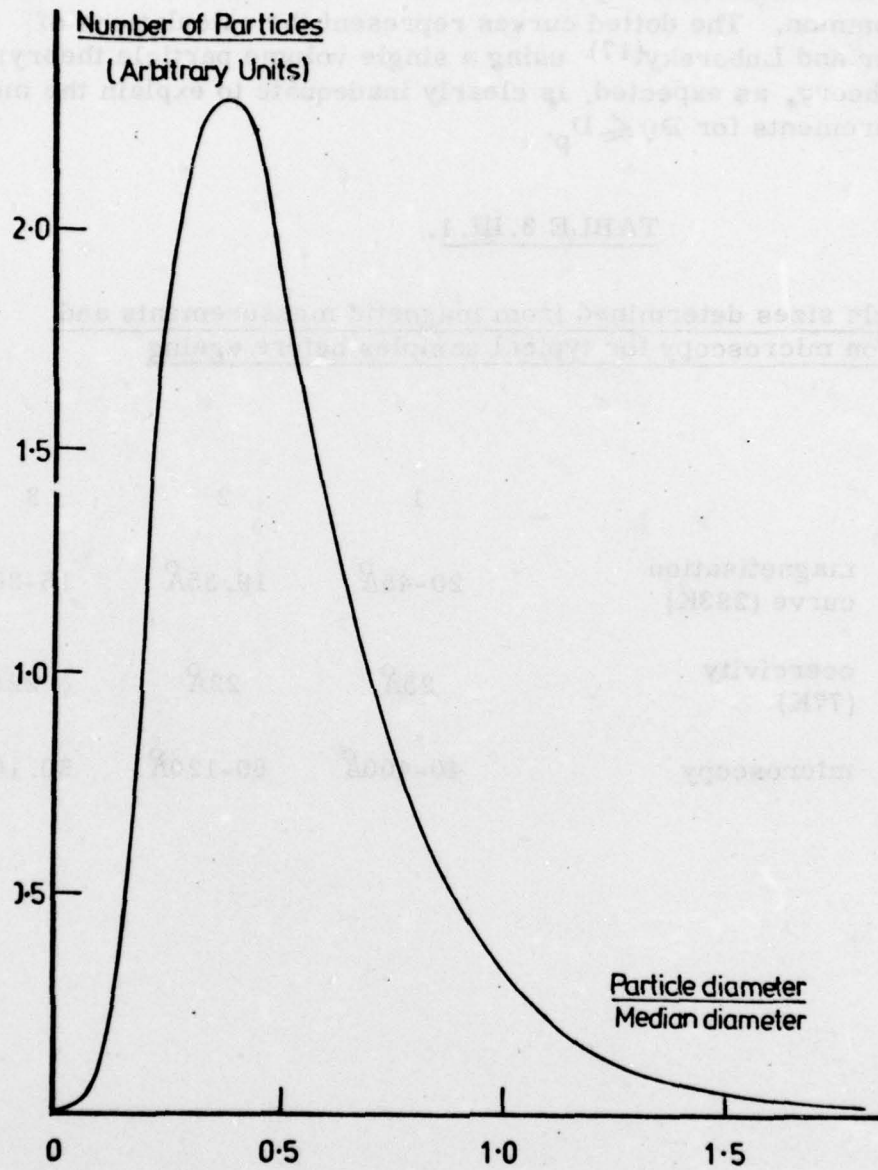


Figure 3.III.4. Log-normal distribution of volume fraction

fraction are compared with the experimental values in Figure 3.III.5. and 3.III.6. The agreement is very satisfactory and much better than other forms of distribution. This result is not so surprising since there is considerable experimental evidence that such distributions are common. The dotted curves represent the calculations of Kneller and Luborsky<sup>(17)</sup> using a single volume particle theory. This theory, as expected, is clearly inadequate to explain the magnetic measurements for  $D_V \leq D_P$ .

TABLE 3.III.1.

Particle sizes determined from magnetic measurements and electron microscopy for typical samples before ageing

	1	2	3
(a) magnetisation curve (293K)	20-45Å	19.35Å	15-30Å
(b) coercivity (77K)	25Å	22Å	22Å
(c) microscopy	40-400Å	60-120Å	30.100Å

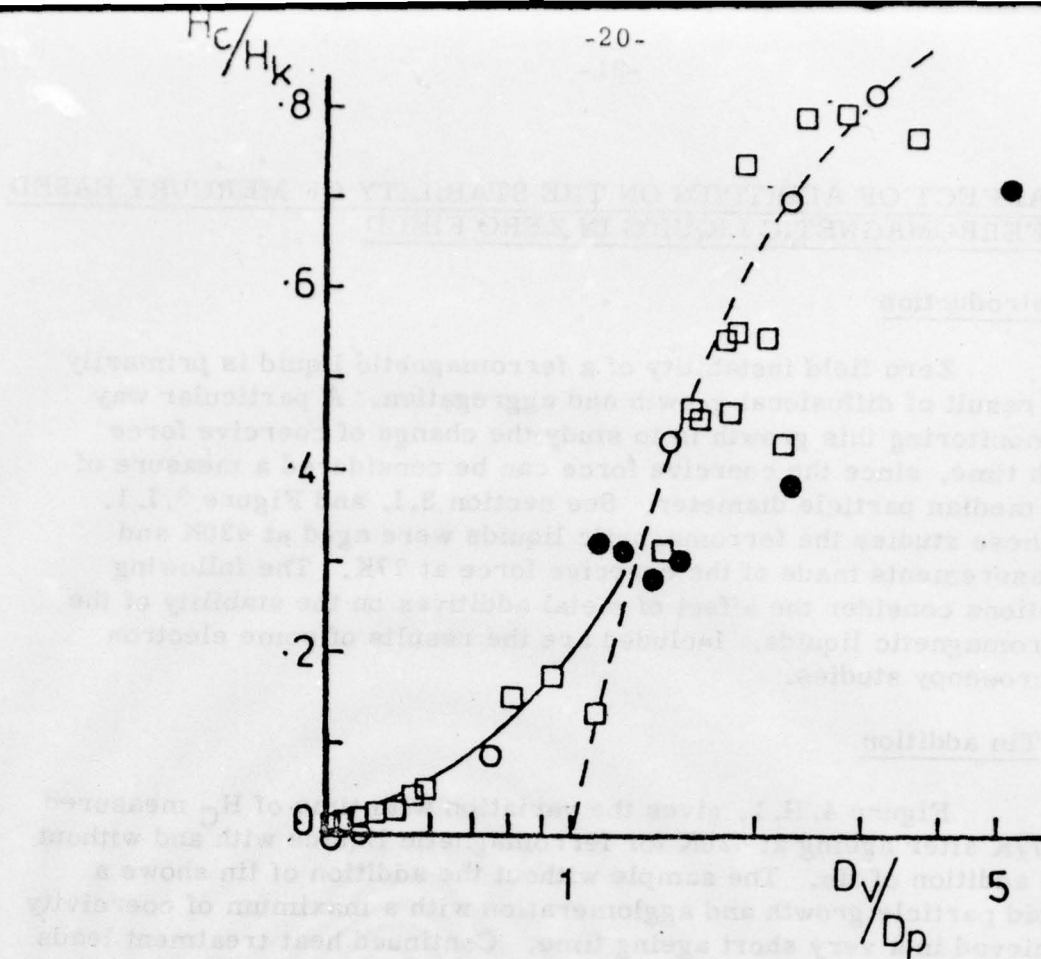


Figure 3.III.5. Coercivity  $H_C$  as a function of particle diameter  $D_V$ . ( $H_K$  is the anisotropy field and  $D_P$  the critical diameter for superparamagnetic behaviour).

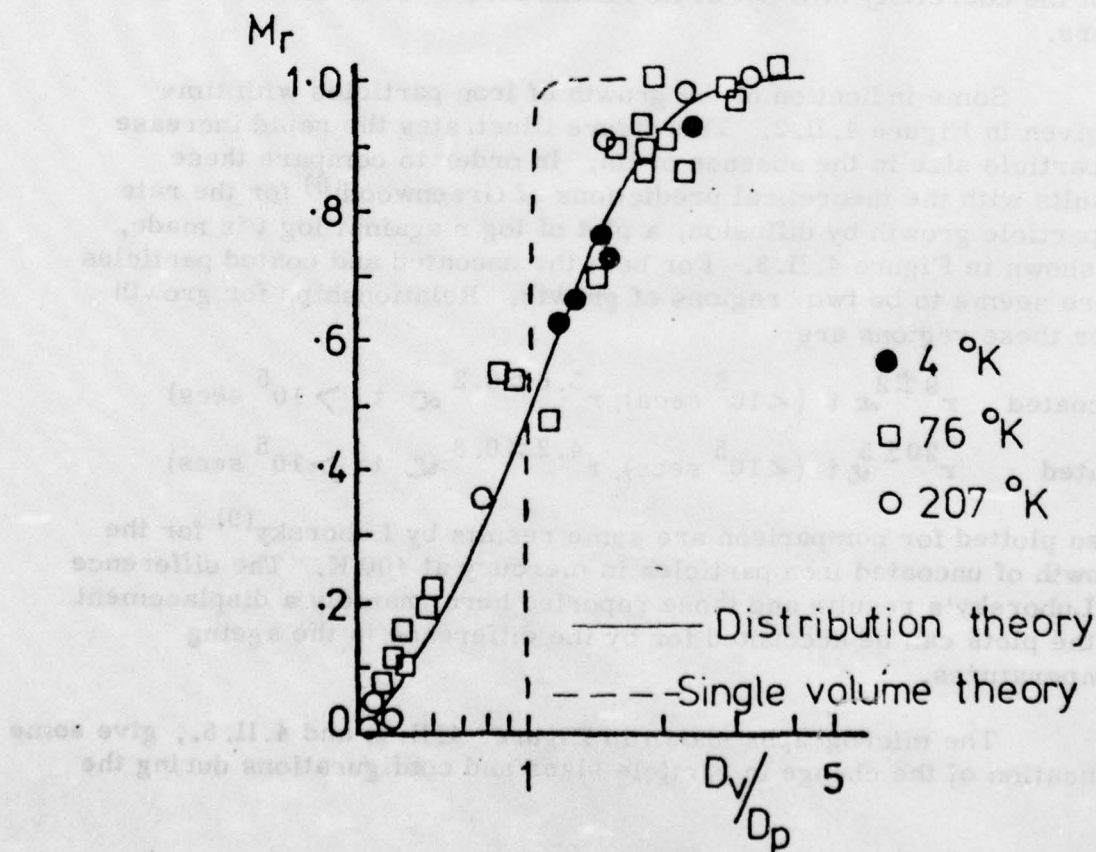


Figure 3.III.6. Reduced remanence  $M_r$  as a function of

#### 4 AFFECT OF ADDITIVES ON THE STABILITY OF MERCURY BASED FERROMAGNETIC LIQUIDS IN ZERO FIELD

##### I Introduction

Zero field instability of a ferromagnetic liquid is primarily the result of diffusional growth and aggregation. A particular way of monitoring this growth is to study the change of coercive force with time, since the coercive force can be considered a measure of the median particle diameter. See section 3.I. and Figure 3.I.1. In these studies the ferromagnetic liquids were aged at 420K and measurements made of the coercive force at 77K. The following sections consider the affect of metal additives on the stability of the ferromagnetic liquids. Included are the results of some electron microscopy studies.

##### II Tin addition

Figure 4.II.1. gives the variation with time of  $H_C$  measured at 77K after ageing at 420K for ferromagnetic liquids with and without the addition of tin. The sample without the addition of tin shows a rapid particle growth and agglomeration with a maximum of coercivity achieved in a very short ageing time. Continued heat treatment leads to a reduction in coercivity indicating particle growth to polydomain size. In contrast to this the sample with the addition of tin, i.e. a coated sample shows a substantially lower coercivity and hence growth, with the coercivity still not at its maximum ( $\sim 1000$  oe) after 1500 hours.

Some indication of the growth of iron particles with time is given in Figure 4.II.2. This figure illustrates the rapid increase in particle size in the absence of tin. In order to compare these results with the theoretical predictions of Greenwood<sup>(8)</sup> for the rate of particle growth by diffusion, a plot of  $\log r$  against  $\log t$  is made, as shown in Figure 4.II.3. For both the uncoated and coated particles there seems to be two regions of growth. Relationships for growth over these regions are

$$\begin{array}{ll} \text{uncoated} & r^{9 \pm 2} \propto t (< 10^5 \text{ secs}); r^{5.6 \pm 0.2} \propto t (> 10^5 \text{ secs}) \\ \text{coated} & r^{20 \pm 5} \propto t (< 10^5 \text{ secs}); r^{4.2 \pm 0.8} \propto t (> 10^5 \text{ secs}) \end{array}$$

Also plotted for comparison are some results by Luborsky<sup>(9)</sup> for the growth of uncoated iron particles in mercury at 400 K. The difference in Luborsky's results and those reported here, namely a displacement in the plots can be accounted for by the difference in the ageing temperatures.

The micrographs shown in Figures 4.II.4. and 4.II.5., give some indication of the change in particle sizes and configurations during the

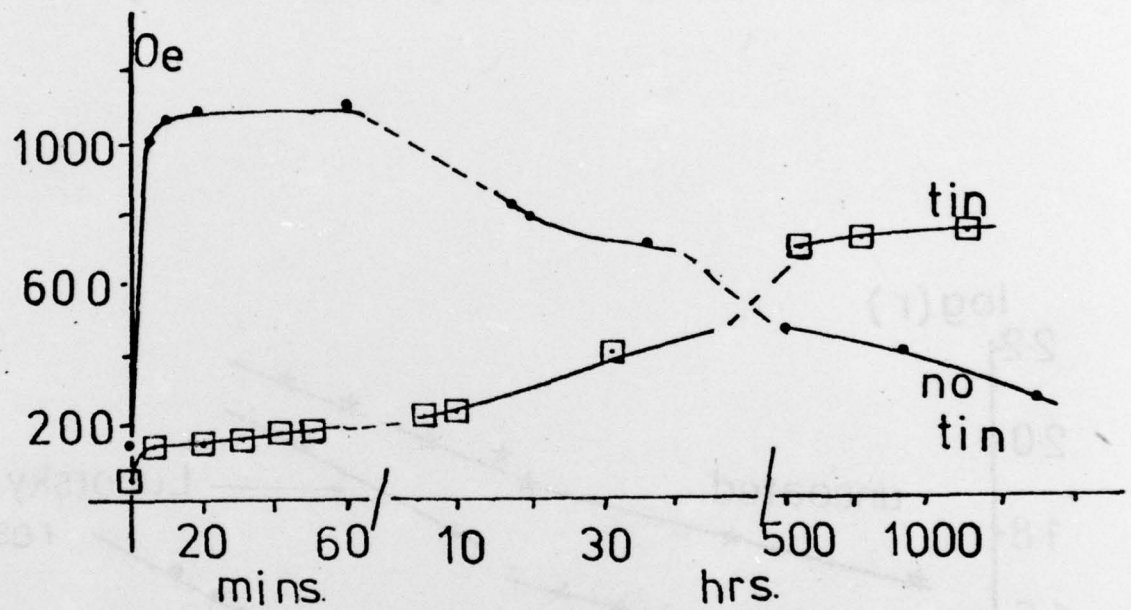


Figure 4.II.1. : Effect of tin addition on Coercivity ageing curves

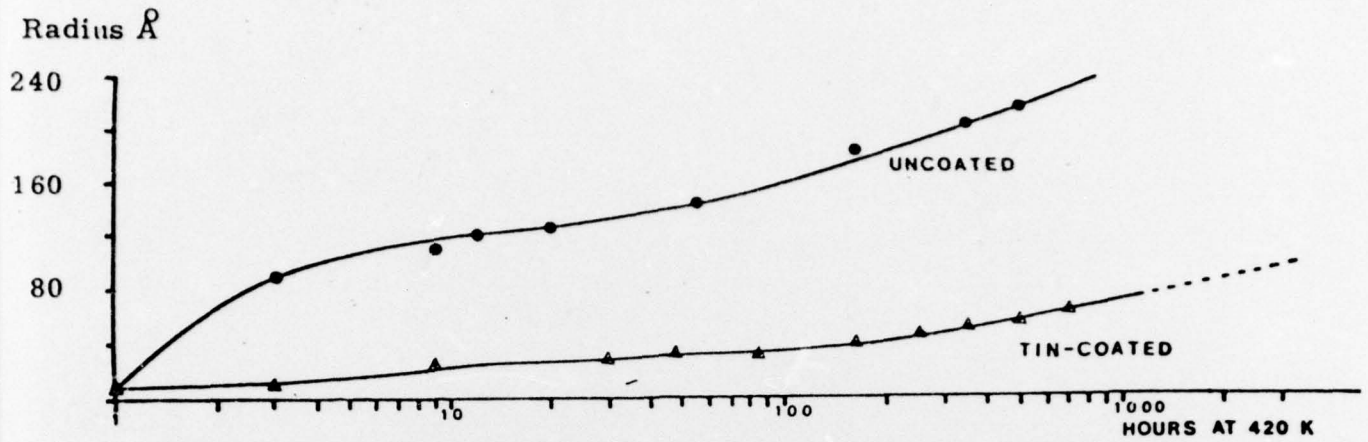


Figure 4.II.2. Tin stabilisation of iron particles in mercury

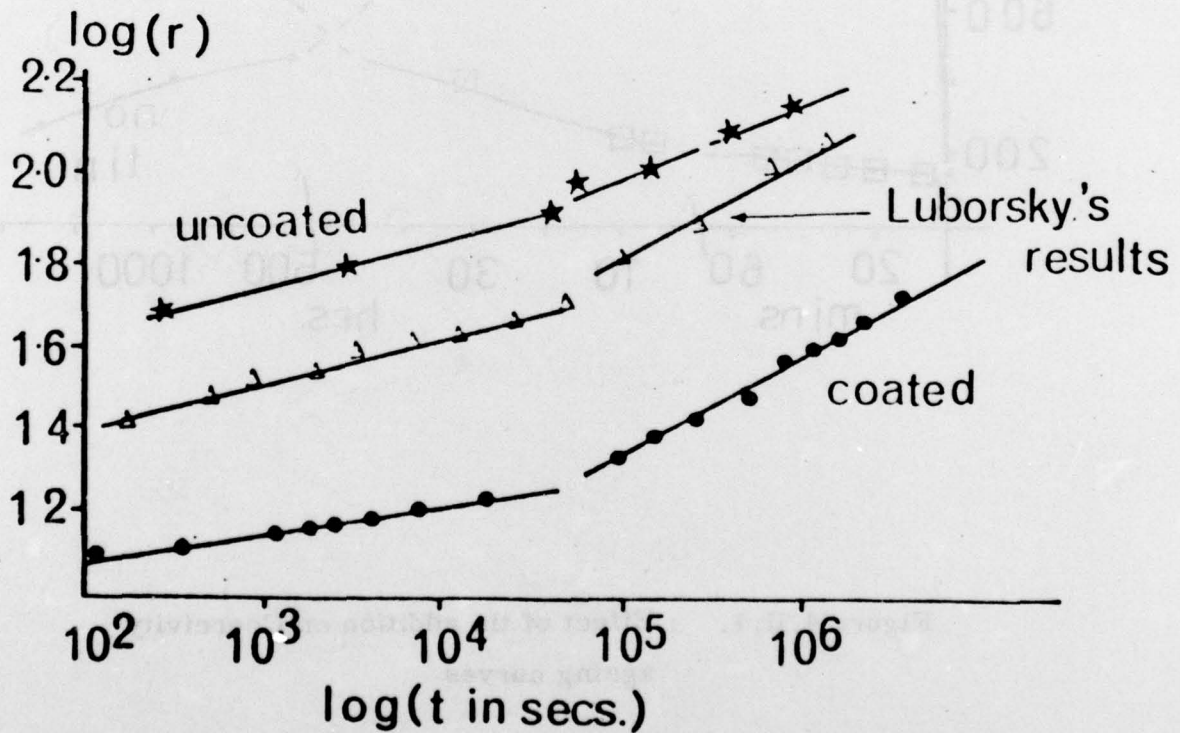


Figure 4.II.3. Growth of particles with time on a logarithmic scale

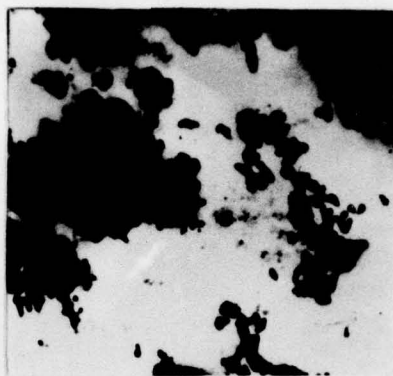


Figure 4.11.4. Clusters of iron particles in sample with tin addition after 60 hours ageing.



Figure 4.11.5. Clusters of iron particles in sample with tin addition after 330 hours ageing.

heat treatment. Figure 4.II.4. shows particles taken from a tin-coated sample aged for 60 hours with a coercivity of 600 oe. The average particle radius is approximately  $50 \text{ \AA}$ . Figure 4.II.5. shows a similar sample after 330 hours ageing. This has a coercivity of 740 oe and the average radius is  $90 \text{ \AA}$ . Both micrographs show evidence of clustering. No clusters were found in the micrographs taken of particles from the freshly prepared ferrofluids.

### III Sodium addition

The presence of tin in a ferromagnetic liquid consisting of iron particles in mercury leads to a dramatic increase in the stability of the system. This increase has been attributed to the inhibition of particle growth as a result of diffusion. However, agglomeration of particles is still a problem (Figure 4.II.4). If this agglomeration is due to some van der Waals' type interaction as mentioned in Section 1.II.2. then such an interaction may be overcome if some repulsive interactions between the particles can be introduced.

A possible source of repulsion between particles is now outlined. Electron charge transfer takes place across the interface of two metals having different Fermi energies. The transfer rapidly reaches an equilibrium and the quantity and extent of the charge distributed across the boundary depends on the Fermi energies and work functions respectively. Such a situation would arise at the ferromagnetic particle/metallic liquid interface in a ferromagnetic liquid. The 'space' charge would reside around the particle and would oppose particle contact if the extent of the charge distributions were appreciable.

Ehrenberg<sup>(18)</sup> has discussed the problem of charge transfer between metals in 'contact' and a diagrammatic representation of the variation of the Fermi energy at a spherically symmetric interface is shown in Figures 4.III.1. and 4.III.2. The distribution is obtained by determining the charge transfer as the two metals are brought together. The theoretical analysis breaks down at zero contact and this situation has to be examined by extrapolation. Solutions of the three dimensional Poisson's equation show that the charge density changes exponentially in the vicinity of the particle-liquid interface. This change in charge density is significant for a tin/sodium interface at a distance of  $5 \text{ \AA}$  from the boundary. For the situation at an iron/mercury interface the effect would be minimal (Figure 4.III.1).

The change in Fermi energy due to charge transfer at the interface can be written

$$Y = Y_1 \exp \alpha r$$

where  $r$  is the radial extent of the charge variation,  $\alpha$  is proportional to  $E_f^{\dagger}$  and  $Y_1$  is proportional to  $\phi_2 - \phi_1$ .  $\phi_1$  and  $\phi_2$  are the respective work functions for the two metals.

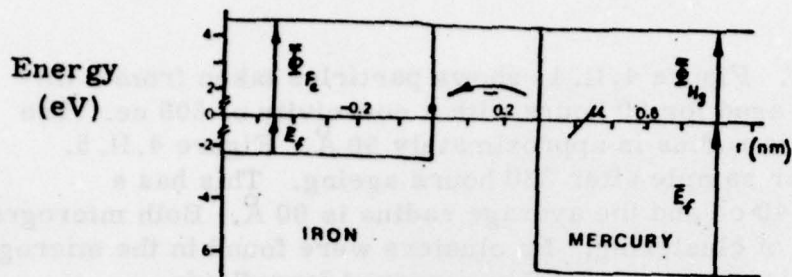


Figure 4.III.1. The change in energy and charge density at an iron/mercury interface (after Ehrenberg)  $\Phi$  and  $\bar{E}_f$  refer to the bulk values of work function and Fermi energy respectively

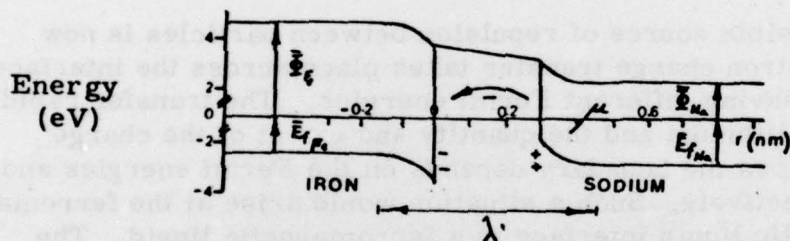


Figure 4.III.2. The change in energy and charge density at a sodium/iron interface (after Ehrenberg<sup>(18)</sup>)  $\lambda$  = Charge layer width

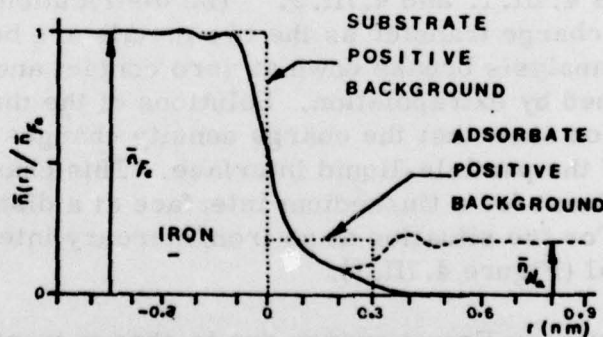


Figure 4.III.3. Electron density distribution  $\bar{n}(r)$  for a monolayer of sodium — (after Lang<sup>(19)</sup>) (proposed distribution for more than a monolayer - - -)

An alternative approach to the problem is based on the work of Lang<sup>(19)</sup> who considers the effect of metal coatings on the work functions of surfaces. This treatment enables the charge density at zero separation to be examined without recourse to extrapolation. Coupled with Ehrenberg's prediction the overall view of the charge distribution can be examined on a qualitative basis and this is illustrated in Figure 4.III.3. It may, therefore, be argued that the spatial extent and magnitude of the 'space' charge at the particle/liquid interface can be controlled by the selection of the coating material. In order to produce a significant repulsive force between particles a large 'space' charge would be needed. Thus a material with a work function very different from iron, tin or mercury would be best and in this respect sodium metal  $\phi \sim 2.4\text{eV}$  (or caesium  $\phi \sim 2.14\text{eV}$ ) would seem to be suitable.

Magnetisation measurements have been taken at 293K and 77K on ferromagnetic liquids of iron in mercury containing tin in sufficient quantity to produce a monolayer on the iron particles and in addition an excess of sodium. All the liquids so prepared exhibit magnetisation curves similar to those in Figure 3.III.1. and 3.III.2., i.e. at room temperature the sample is clearly superparamagnetic and at 77K is ferromagnetic. All liquids have been aged progressively by heating to 420K for periods up to several months.

The variation of particle size with ageing time for several liquids in which sodium has been added are shown in Figure 4.III.4. The figure indicates that particle growth has been inhibited in the long term, the particle diameter of 50 Å remaining constant over several months. (c.f. Figure 4.II.2). Although long term stability would appear to have been achieved there is still an initial growth.

An alternative approach to the problem is based on the work of Langmuir<sup>1</sup> who considers the effect of metal coating on the work function of surfaces. This treatment enables the change in density of void separation to be examined without recourse to equilibrium. Coupled with Whipple's<sup>2</sup> prediction of the overall view of the change in evaporation rate, this can be examined on a quantitative basis and this is illustrated in Figure 4.III.4. It may, therefore, be argued that the spatial extent and character of the voids change at the particle surface interface can be controlled by the selection of the coating material. In order to produce a significant separation force between particles a large space charge would be needed. Thus a material with a work function very different from tin or mercury would be used and in this respect sodium metal ( $\phi \sim 2.4$  eV for sodium,  $\phi \sim 4.1$  eV for tin) would seem to be suitable.

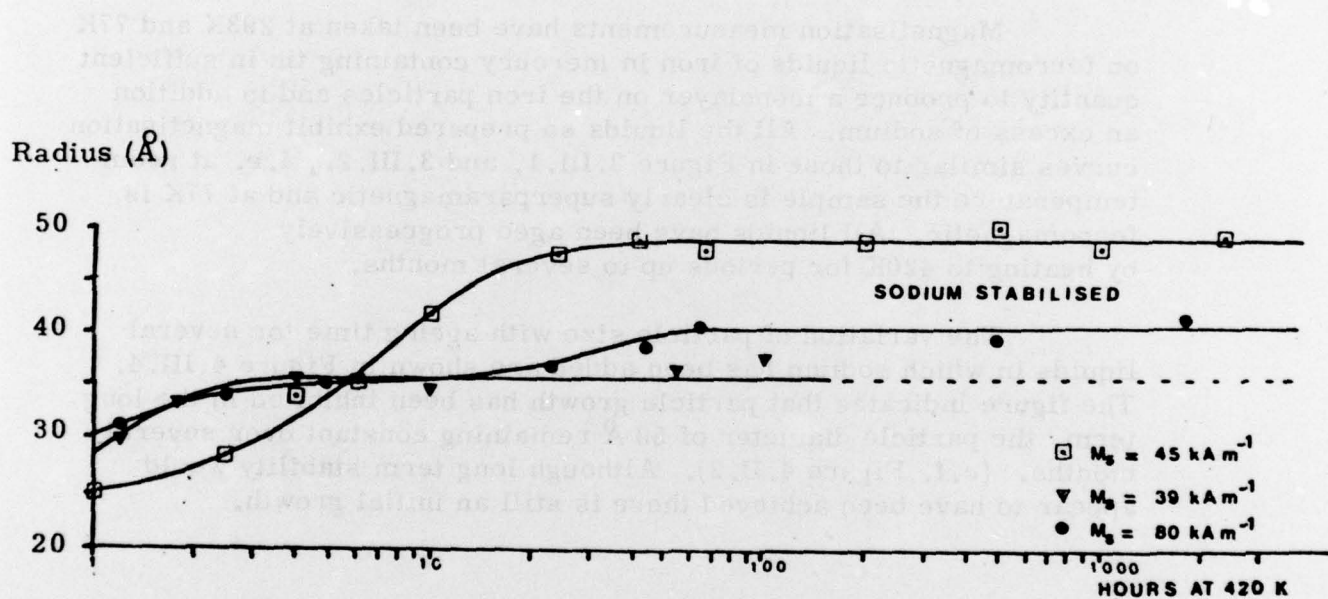


Figure 4.III.4. Sodium stabilisation of tin-coated iron particles in mercury

## 5 STABILITY OF METALLIC FERROMAGNETIC LIQUIDS IN HIGH MAGNETIC FIELDS

Studies of the stability were confined to those liquids having long term stability in zero magnetic field, namely those ferromagnetic liquids containing sodium.

Using the theory as outlined in Section 1.II.4. and considering as a criterion indicative of magnetic separation a concentration gradient  $\frac{\nabla n}{n} = 1\text{cm}^{-1}$  which corresponds

to 100% change of mean particle concentration per centimetre, then the stable metallic ferromagnetic liquids produced to date should possess a stability in high magnetic fields which would enable them to be used in seals and energy conversion systems.

The median diameter of the iron particles to be found in the long term stable liquids is approximately  $50\text{\AA}$ . For particles of this size possessing a magnetisation  $M_s = 21,580$  gauss, Figure 1.II.2. indicates that for  $H = 10^4$  oersted/cm, the time for particles to move 1 cm would be  $10^3$  seconds, i.e. 16 minutes and even for  $H = 10^5$  oersted/cm, the time would still be 100 secs.

Experimental studies on the long term stable liquids indicate that in field gradients comparable to those mentioned above, the time for the particle to move 1 cm was very much less than 1 sec. In fact an almost instantaneous magnetic concentration of the particles occurred resulting in a fluid possessing an approximately 3 fold increase in concentration of particles and a marked increase in viscosity. The remaining fluid appeared to be non-magnetic and had a similar viscosity to that of mercury. Continuous application of a strong field to the magnetically concentrated fraction ultimately lead to a further concentration resulting in a very viscous magnetic slurry.

Clearly the theory presented in Section 1.II.4. whilst being adequate to explain the properties of the non-metallic ferromagnetic liquids, appears to be totally inadequate by itself to explain the observations on metallic ferromagnetic liquids.

## 6 DISCUSSION

The stability of a suspension of iron particles in mercury in zero magnetic field has been shown to be improved by the addition of tin. The tin provides a coating around the iron particles which limits diffusional growth. However, long term stability is not achieved by the addition of tin alone. Long term stability has been achieved by the addition of sodium to the ferromagnetic liquid containing tin. This has been attributed to the presence of a space charge, i.e. a charge transfer at the particle/liquid interface, opposing particle contact. The equation in section 4.III. would indicate that to obtain effective charge transfer the work functions of the metallic liquid and particle must differ appreciably. For elements such as tin, mercury and iron these differences are not sufficiently marked to be noticeable. For sodium the work function is significantly smaller than for mercury and the charge transfer is expected to be appreciable.

Bennett and Falicov<sup>(20)</sup> have discussed various types of adsorptions qualitatively. Typically for the alkali metals they predict for a normal external field of  $0.1 \text{ nV m}^{-1}$  a charge transfer of  $0.37q$  ( $0 < |q| < e$ ) per adsorbate - substrate atom pair where the adsorbate-substrate distance is approximately  $3\text{\AA}$ . The corresponding electric fields in the systems discussed in this paper may be thought to have their origins in the difference of the adsorbate and substrate work functions.

When sodium is added in excess to the mercury based ferromagnetic liquid containing tin it is not known whether the sodium remaining entirely in the mercury or if some or all of the sodium forms a coating about the particle. It is a consequence of the Lang<sup>(19)</sup> treatment that the charge transfer at the interface would be most noticeable for a sodium coating, the effect becoming much reduced as the concentrations of the sodium in the mercury is raised. The result of raising the sodium concentration is expected to change the mercury work function (Namamoto, Susa, Kawabe and Okano<sup>(21)</sup>) and hence possibly reduce the difference between it and that of the sodium coating, resulting in a reduction in the space charge.

It would be interesting, therefore, to examine the relationship between the sodium concentration and fluid stability since it is possible that optimum conditions for stability have not yet been achieved in our systems.

The problem of stability of iron particles in mercury have been overcome in zero magnetic field. However, initial

THE EFFECT OF A PARTICLE SIZE DISTRIBUTION ON THE COERCIVITY AND REMANENCE OF A FINE PARTICLE SYSTEM

experiments on these stable ferromagnetic liquids in high magnetic fields indicate that the theory as outlined in Section 1.II.4. is not adequate in itself to explain the very rapid movement of particles through the mercury. See section 5. At the present time it is not known whether this phenomenon is the result of magnetic interactions between the particles, e.g. chaining or is associated with the properties of liquid mercury.

Clearly this problem is of considerable importance and needs to be solved if metallic ferromagnetic liquids are to be used in high magnetic fields, as for example in an energy convertor. In order to resolve this problem studies are in progress on ferromagnetic liquids with gallium as a carrier and liquids containing cobalt particles in mercury as carrier.

$$\chi = \frac{N}{V} \frac{H_c}{H} \frac{1}{1 + \frac{H_c}{H}} \quad (1)$$

$$\chi = \frac{N}{V} \frac{H_c}{H} \frac{1}{1 + \frac{H_c}{H}} \quad (2)$$

$$\chi = \frac{N}{V} \frac{H_c}{H} \frac{1}{1 + \frac{H_c}{H}} \quad (3)$$

An expression for the magnetization of ferromagnetic particles is then given by substituting for  $\chi$  from (3) into (2).

The theory applies to an assembly of particles with easy axes aligned and parallel to the field. Experimentally, however, the easy axes are randomly oriented. Therefore such good agreement between theory and experiment might not have been expected. Tolle [34] has given theoretical calculations of  $H_c/H$  against  $D/D_p$  for a single particle size, randomly oriented system. This is found to differ very little in form from the aligned case, although they do differ in magnitude, the maximum value of  $H_c/H$  being equal to 1 (aligned), and 0.473 (random). To show the similarity between the two cases, the random orientation theory was compared with the expression

$$H_c/H = B(1 - \sqrt{V/V_p}) \quad (4)$$

(4) is the single particle volume expression for the aligned case, but including a constant  $B$ . The two curves were found to be similar for

# THE EFFECT OF A PARTICLE SIZE DISTRIBUTION ON THE COERCIVITY AND REMANENCE OF A FINE PARTICLE SYSTEM

$M_H$ , the magnetisation in a field  $H$  divided by  $M_s$ , the sample saturation magnetisation is given by

$$M_H = \int F_H(D) f(D) dD \quad (1)$$

Where the integration is performed over the distribution defined by  $f(D)$ .  $F_H(D)$  is an expression relating magnetisation and field for particles of diameter  $D$ . For  $D < D_p$ ,  $F_H(D)$  is the Langevin function

$$F_H(D) = \coth b - 1/b \quad (2)$$

( $b = 1 \pi H D^3 / 6 k T$ , and  $M_s = 4 \pi M_s$  is the saturation magnetisation of the bulk material). For  $D \geq D_p$ , the magnetisation becomes time dependent and it can be shown that

$$F_H(D) = 2 \exp(-t/\tau) - 1 \quad (3)$$

This is valid at high fields, and the behaviour of the magnetisation at low fields will be discussed in a future publication [22]  $\tau$  is a relaxation time given by Brown's equation [23]

$$t/\tau = t \gamma_0 H_K \sqrt{a} (1-h^2) \exp(-a(1+h^2)) [(1-h)e^b + (1+h)e^{-b}] / 2\sqrt{\pi} \quad (4)$$

Here,  $a = KV/kT$ ,  $V$  is the particle volume,  $\gamma_0$  is the gyromagnetic ratio,  $h = H/H_K$ , and  $H_K = 2K/I_s$ .  $K$  is the anisotropy constant of the particle, which can arise from crystalline and / or shape anisotropy. From the experimental data, Kneller and Luborsky have obtained a value for the critical volume in zero field. Theoretically,  $V_p$  is given by setting  $t/\tau = 1$  and  $h = 0$  in (4). Thus

$$t \gamma_0 H_K / \sqrt{\pi} = \exp(a_p) / \sqrt{a_p} \quad (a_p = KV_p/kT) \quad (5)$$

substituting (5) into (4) gives

$$t/\tau = (a/a_p) (1-h^2) \exp(a_p - a(1+h^2)) [(1-h)e^b + (1+h)e^{-b}] / 2 \quad (6)$$

An expression for the magnetisation of ferromagnetic particles is then given by substituting for  $t/\tau$  from (6) into (3).

The theory applies to an assembly of particles with easy axes aligned and parallel to the field. Experimentally, however, the easy axes are randomly oriented. Therefore such good agreement between theory and experiment might not have been expected. Joffe [24] has given theoretical calculations of  $H_c/H_K$  against  $D/D_p$  for a single particle size, randomly oriented system. This is found to differ very little in form from the aligned case, although they do differ in magnitude, the maximum value of  $H_c/H_K$  being equal to 1 (aligned), and 0.479 (random). To show the similarity between the two cases, the random orientation theory was compared with the expression

$$H_c/H_K = B(1 - \sqrt{V_p/V}) \quad (7)$$

(7) is the single particle volume expression for the aligned case, but including a constant,  $B$ . The two curves were found to be similar for  $B = 0.61$ .

## REFERENCES

1. E L Resler Jr and R F Rosensweig : AIAA Journal 2 No 8, p 1418 (1964).
2. R E Rosensweig, J W Nestor and R S Timmins : A I Ch E - I Chem E Symposium series No 5, p 5:104 (1965).
3. B Chu, Chapters 4 and 5 'Molecular Forces', pub Wiley (1967).
4. J H de Boer, Trans Faraday Soc, 32, p 10 (1936).
5. H C Hamaker : Rec Trav Chim, 55, p 1015 (1936).
6. E M Lifshitz, J Expt Theor Phys (USSR) 29, p 94 (1955).
7. M J Sparnaay, Physica, 24, p 262 (1958).
8. G W Greenwood, Acta Met, 4, p 243 (1956).
9. F E Luborsky, Journ Phys Chem, 61, p 1336 (1957).
10. F E Luborsky, J Phy Chem, 62, p 1131 (1958).
11. R B Falk, F E Luborsky, Trans Met Soc, AIME 233, p 2079 (1965).
12. C P Bean, J D Livingston, J A P Suppl, 30, No 4, p 1205 (1959).
13. C P Bean, I S Jacobs, J A P, 27, No 12, p 1448 (1956).
14. F E Luborsky, J A P, Suppl, 32, p 1715 (1961).
15. L Weil, J Chim Phys, 51, p 715 (1954).
16. L Weil, L Gruner : Compt Rend, 243, p 1629 (1956).
17. Kneller & Luborsky, J Appl Phys, 34, 656 (1963).
18. W Ehrenberg, 'Electrical Conduction in Semiconductors and Metals' Chap 11, Oxford Press (1958).
19. N D Lang, Phys Rev, 4, No 12, 4234 (1971).
20. A J Bennett and L M Falicov, Phys Rev, 151, No 2, 512 (1966).
21. S Yamamoto, K Susa, U Kawabe and H Okano, J Appl Phys Supp 2, Pt 2, 209 (1974).
22. R W Chantrell (to be published).
23. W F Brown Jr, Phys Rev 130, 5, 1677 (1963).
24. I Joffe, J Phy C, 2, 1537 (1969).

Publications arising from the work sponsored by the U S Army

1. 'The Long Term Stability of Mercury Based Ferromagnetic Liquids', P L Windle, J Popplewell and S W Charles, IEE Transactions on Magnetics, Vol 11, 1367-1369, 1975.
2. 'The Long Term Stability of Magnetic Liquids for Energy Conversion Devices', J Popplewell and S W Charles, Energy Conversion. Accepted for publication in early 1977.
3. 'The Magnetic Properties of Ferromagnetic Liquids Containing Iron Particles in Mercury', J Popplewell and S W Charles, A paper presented at the Joint MMM-Intermag Conference June 1976 and to be published 1977.
4. 'The Long Term Stability of Metallic Ferromagnetic Liquids', J Popplewell, S W Charles and S R Hoon, A paper published September 1976 by the IEE and delivered at the 2nd Conference on 'Advances in Magnetic Materials and their Applications'.
5. 'The Effect of a Particle Size Distribution on the Coercivity and Remanence of a Fine Particle System', R W Chantrell, J Popplewell and S W Charles, A paper to be published in early 1977 and delivered at the International Conference on Magnetism in Amsterdam; September 1976.